ZEOLITES PROCEDURE

Zeolites are three-dimensional, crystalline networks of AlO4- and SiO4 tetrahedra. Their crystallization is often a nucleation-controlled process from a gel and the structure that crystallizes depends on the cations present. “A multitude of commercial processes have been developed that exploit size exclusion and selective molecular diffusivity properties based upon the nanosize pore and channel structure of zeolites… The demand for two C8 isomers, paraxylene and orthoxylene, is much greater than that for the C8 isomers metaxylene and ethylbenzene. H-ZSM5 with its 0.6 nm pore size has the ability to isomerize xylenes with little cracking of the feedstock. A second crucial property is that paraxylene has a much higher diffusivity in H-ZSM5 than do the other xylene isomers. This means that the paraxylene molecules can more easily diffuse out of the zeolite crystal, whereas the ortho and metaxylene isomers are effectively trapped within the pores.

ZSM-5, Zeolite Socony, is a catalyst first made by Argauer and Landolt in 1972. It is a medium pore zeolite with channels defined by ten-membered rings. The synthesis involves three different solutions. The first solution is the source of alumina, sodium ions, and hydroxide ions; in the presence of excess base the alumina will form soluble Al(OH)4- ions. The second solution has the tetrapropylammonium cation that acts as a templating agent. The third solution is the source of silica, one of the basic building blocks for the framework structure of a zeolite. Mixing the three solutions produces supersaturated tetrapropylammonium ZSM-5, which can be heated to recrystallize and produce a solid. In subsequent steps the organic templating agent is removed and the zeolite converted to its acid form.

PART I

Place 25 mL water in a large weighing boat, prepare sodium aluminate, NaAlO2, by adding 0.30 g Al2O3 (0.0018 mol aluminum oxide, activated, neutral, Brockman I, 150 mesh) and 2 pellets NaOH (~0.20 g or 0.0050 mol) and stirring to dissolve the NaOH. Add an additional 2.95 g NaOH (0.075 mole) and stir to dissolve the NaOH. Put 50 mL water in a second weighing boat. Add 1.7 mL of 96% H2SO4 (0.030 mole) and 4.0 g tetrapropylammonium bromide (0.015 mole). Stir until everything has dissolved. Place 24 mL of silica-sol (0.15 mol LUDOX HS-30 colloidal silica, 30 wt% SiO2) in a polypropylene screw top jar. Simultaneously pour in the contents of the two weighing boats, cap, and shake vigorously for 5 minutes to form a gel. The pH should be in the 11-12 range as measured by pH paper.Stir for another 30 minutes. Place the tightly closed screw-top jar in an oven at ~95°C for a week.

PART II

. After a week of heating the gelatinous appearance should be completely gone, leaving a clear solution with a fine white solid at the bottom. Remove the jar from the oven and open the cap while the solution is still hot. Pour off the liquid. Gravity filter the product and rinse with water until the pH is about 8. (This step takes a while but suction filtration is even slower since the filter gets clogged.) Let the solid air dry. Fill an alundum boat with the TPA-ZSM5. Load the boat into a tube furnace. Run nitrogen through the tube and into a bubbler. Maintain a slow flow.Heat at a rate of 4°C/min to 100°C, then increase at 10°C/min to 500°C. Maintain at 500°C for 2 hours then cool to room temperature. As the organic templating agent thermally decomposes the product may darken. Obtain the X-ray powder diffraction spectrum of Na-ZSM-5 by scanning from 5 to 28 degrees. Compare with the expected peaks at 11.1 (s), 10.0 (s), 3.85 (vs) and 3.71(s) Å.

PART III

The sodium form of the zeolite is converted to the acid form by placing it in a 100 mL beaker and stirring with a 1.0 M (NH4)2SO4 solution (10 mL/g zeolite) for 10 to 15 minutes at ambient temperature. The zeolite is transferred with the aid of a wash bottle and collected by vacuum filtration. Wash with distilled water until the filtrate is free of sulfate anions as indicated by adding BaCl2 dropwise and looking for a BaSO4 precipitate. (A positive test is shown.) Wash with distilled water until the filtrate is free of sulfate anions as indicated by adding BaCl2 dropwise and looking for a BaSO4 precipitate. (A negative test is shown.) Rinse with acetone to dry the solid. Transfer the dried solid to an alundum boat in a tube furnace. Heat the materials in air at 500°C for a period of at least 3 hours. (Do not pass nitrogen gas over the solid – the presence of oxygen is essential for the conversion.) Cool the material under a stream of nitrogen. Store in a desiccator to preserve the acid hydrogen form of the zeolite.

PART IV

Xylene isomerization is carried out in a fumehood, using a catalytic reactor.

Place a known mass of H-ZSM-5 catalyst in the fritted adapter, followed by glass wool. (Do not use too much glass wool or pack the sample too tightly or the xylene will be unable to pass through. Place 15 mL of o-xylene in the reflux flask. Flow nitrogen gas through apparatus (approximately 6-10 psi is required) at a low to moderate flow rate as indicated by the bubbler. Heat the tube furnace to 425°C and heat the xylene to its boiling temperature (140°C). Nitrogen acts as a carrier gas to transport the hot o-xylene vapor through the catalyst. Place the collection flask in an ice bath to ensure condensation of the xylenes. Obtain a 1H NMR spectrum of both the initial o-xylene and the product. Use integration to determine the extent of conversion to p-xylene.